

PATENT SPECIFICATION



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COMPLETE SPECIFICATION

Improvements in or relating to the Crystallisation of Nitrates from Nitric Acid Solutions of Calcium Phosphate

We, NORSK HYDRO-ELEKTRISK KVELSTOFKEMISKELSKAB, a Norwegian Body Corporate, of 7, Solligaten, Oslo, Norway, do hereby declare the invention, for which we pray 5 that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

By a known method raw phosphates are 10 converted into soluble form by treatment with nitric acid, whereby a solution is obtained which contains calcium nitrate, free phosphoric acid and some excess of nitric acid. The major part of the calcium nitrate 15 is caused to crystallise out by cooling said solution, whereupon the crystallised nitrate is separated from the mother lye.

Raw phosphate contains as a rule quite large quantities of impurities which are in- 20 soluble in nitric acid. These insoluble impurities which are present in extremely finely divided form and cause in the technical application of the process such great difficulties that a satisfactory procedure involves in 25 practice many problems. Attempts have been made to solve these problems in various ways. Thus it has been proposed to filter off these finely divided and insoluble impurities while the solution is still hot, that is, 30 before crystallisation occurs, but it has been found that the solution is not suitable for filtration. The strongly acid hot solution has an extremely corrosive effect on the apparatus and the filter material, and in addition the filter very quickly gets clogged. Nor 35 is removal of the finely divided and insoluble substances by decantation, for example, by means of Dorr apparatus, feasible. The impurities are so finely divided that settling 40 within a reasonable time is difficult to carry out, and furthermore, this lengthy process must in any case be performed without cooling the liquid, both because it is important that the solution shall not become too vis- 45 cous, and in order to prevent crystallisation

while settling is going on.

On account of these circumstances it is proposed to cool the solution and crystallise out the calcium nitrate without previous separation of the finely divided and insoluble 50 impurities. It is evident that it is not a simple matter to carry out such a process in a satisfactory manner, because it is necessary to avoid the effect that the calcium nitrate which is to be separated from the mother 55 lye, is contaminated by the insoluble components from the raw phosphate. Attempt has been made to carry out the process without prior separation, by working in the way that crystallisation of the calcium nitrate is 60 carried out in continuously working apparatus in order to obtain well developed calcium nitrate crystals, and to use relatively coarse filtering cloth, or fine-meshed, acid- 65 proof gauze wire, and by this method the result should be that the calcium nitrate crystals are left on the filter cloth, while the mother lye and the insoluble impurities pass through without clogging the filter.

It has been found, however, that when 70 this known and hitherto preferred method is employed in the crystallisation of nitrates, e.g., calcium nitrate tetrahydrate, from nitric acid solutions of raw phosphate, difficulties are always encountered in the filtration of the 75 crystal suspension, as the filter pores are clogged with the effect that filtration soon ceases.

Further, this continuous operation has the drawback that the coating of salt which 80 forms on the cooling surfaces of the apparatus is, for reasons which will be readily understood, difficult to remove without interfering with the continuous operation of the process.

The result of our research and experiments 85 is a new method which can be realised in a simple and thoroughly satisfactory way. We have found that the solution of the very difficult filtration problem depends on the cir- 90

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cumstance that the calcium nitrate crystals formed acquire a specific granular size.

Thus it has been found by the investigations carried out that in order to enable the 5 finely divided insoluble impurities to pass through the filter without clogging it, the maximum granular size of the calcium nitrate crystals must be less than 2.0 mm, while granular sizes lower than 0.5 mm must be 10 avoided, and that in particular the presence of quite small crystals of size 0.1-0.2 mm causes difficulties. The best results in the filtering process are obtained when the maximum granular size of the crystals in the 15 crystal suspension is less than 2.0 mm, and at least 80% by weight of the crystals have a granular size between 0.5 and 1.5 mm, preferably between 0.5 and 1.0 mm.

The reason why the granular size of the 20 calcium nitrate crystals is of such a decisive significance is assumed to be that the very finely divided, insoluble components have a tendency to form a continuous cake or layer with the crystals, when these have not the 25 right size.

We have found that the said granular size and granular size distribution can be obtained when the process is carried out in such a manner that the crystallisation of the 30 nitrate is effected by stages instead of continuously as hitherto and that the crystallisation is initiated in each stage by the addition of seed crystals at a point of time when the temperature of the solution is between 2 35 and 10 degrees centigrade below the saturation temperature. By saturation temperature is meant the temperature at which the solution as a result of the cooling attains saturation with respect to nitrate. This saturation 40 temperature will depend on the concentration and amount of the acid in relation to the lime content of the raw phosphate.

We have found that it is impossible in practice to obtain the said necessary even 45 size of grain and distribution of granular size if the procedure is continuous. Moreover, by working in batches the said difficulties in the removal of the salt coating on the cooling surfaces of the apparatus are also 50 avoided, the salt coating which forms during the cooling period being easily removed by dissolution whenever a new charge is put into the apparatus. The still uncooled solution of the raw phosphate will dissolve the 55 salt coating (of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, for example) which has formed on the cooling surface during the cooling of the previous charge.

Another feature of the invention is that, in order to obtain the said crystal formation, 60 the solution is moderately stirred during the cooling, whereby the formed crystals are just kept suspended in the solution and are not allowed to sink to the bottom of the vessel. Further, after the seed crystals are added, the 65 cooling of the crystal suspension is restricted

in such manner that over-saturation does not increase beyond the value the over-saturation had at the time the seed crystals were added. By over-saturation is meant the content of dissolved nitrate in the lye beyond 70 the content of nitrate at saturation.

The nitrate which has in practice been found most expedient to crystallise, is calcium nitrate tetrahydrate, but the invention comprises also other calcium nitrates. If the 75 solution contains ammonium ions, which will be the case if, for instance, nitric acid containing ammonium nitrate is used for dissolution of the calcium phosphate, the nitrate which is crystallised out will be for ex- 80 ample, the double salt $5\text{Ca}(\text{NO}_3)_2 \cdot \text{NH}_4\text{NO}_3 \cdot 10\text{H}_2\text{O}$.

As seed crystals are used crystals which chiefly contain calcium nitrate, for example calcium nitrate tetrahydrate, in the most 85 finely divided form. A crystallising agent which gives very good results, is, for instance, dust from ordinary nitrate of lime. We have found that this dust which consists of $\text{NH}_4\text{NO}_3 \cdot 5 \text{Ca}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O}$ besides 90 $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and anhydrous $\text{Ca}(\text{NO}_3)_2$, is quite fit as crystallising agent in the crystallisation of nitrate calcium tetrahydrate in spite of the fact that it does not contain the 95 last-mentioned compound.

As will appear from the above, the process aims at the obtaining of crystals which have as far as possible the same granular size within the stated granular size limits. It has been found further, that for attainment of 100 this result it is also important to use seed crystals in most finely divided form, preferably as a fine dust. We have found that it is not the weight and granular size of the seed crystals which are decisive for a successful 105 result of the crystallisation, but the number of grains of the seed crystals per unit volume of crystallising lye, and that for this reason the size of the grains should be as small as possible as otherwise the weight of the seed 110 crystals becomes impractically large.

The crystals will, when the process is carried out in accordance with the invention, start growing at approximately the same moment, and this is one of the reasons why 115 they attain approximately the same size.

The average granular size of the crystals in the crystal suspension can be regulated by varying the degree of super-cooling of the solution at the time the seed crystals are 120 added. Lowering of the temperature at which the seed crystals are added causes increase in the number of grains in the crystal suspension and thereby reduction of the granular size, while, on the other hand, an 125 increase of the temperature causes lowering of the number of grains and increase of the granular size.

The average granular size of the crystals in the crystal suspension can also be regu- 130

lated by varying the number of grains in the seed crystals, as an increase of this number causes a reduction of the size of the grain in the crystal suspension, while a lowering of the number of grains in the seed crystals causes increase of the size of grains in the crystal suspension. We have found, however, that a correct choice of sub-cooling temperature ("seeding temperature") is of greater importance for the average granular size of the crystal mass than the choice of the number of grains of the seed crystals, when the seed crystals are used in dust form. In the latter case the amount of seed substance can be varied in the ratio 1:5 without this having any substantial effect on the filtration properties of the crystal mass.

The raw phosphate is treated with a nitric acid which contains 50-65% by weight HNO_3 . When it is desired to crystallise calcium nitrate tetrahydrate from the solution, it is advantageous to use 55-60%, preferably 58%, by weight nitric acid for dissolution of the raw phosphate, and the seed crystals are added at a point of time when the temperature of the solution is preferably 4 to 7 degrees centigrade below the saturation temperature.

Separation of the crystallised nitrate from the mother lye is effected by filtration, using a coarse-meshed filtering cloth which permits a substantial part of the finely divided and insoluble impurities to pass through the filter together with the phosphoric acid-containing mother lye. Thus this special method of effecting separation of the calcium nitrate from the mother lye does not depend on what is usually meant by filtration, but should rather be described as a straining off. This straining off is advantageously performed on a rotary filter. The size of mesh in the filtering medium should be chosen so that the nitrate crystals are to the greatest possible extent retained without preventing passage of the finely divided and insoluble impurities, that is to say, the mesh should be of the order 0.3-0.5 mm.

The process according to the invention can be carried out with the known natural calcium phosphates, for example, Morocco phosphate, Florida phosphate, and Cola phosphate.

EXAMPLE 1.

1 kgm Cola phosphate (CaO content approximately 51.5% by weight) is dissolved with 1.4 kgms HNO_3 in the form of nitric acid containing 55-60% HNO_3 , preferably 58% HNO_3 . The solution is cooled to a temperature which is 4 degrees centigrade below the saturation temperature, whereupon 0.5 gms calcium nitrate dust is added. The solution is cooled further to a temperature which causes crystallisation of the amount of calcium nitrate it is desired to remove from the lye. This final temperature can,

in the crystallising of the tetrahydrate, for example, be 15°C.

A crystal mass is then obtained having the following granular distribution:

Exceeding 1.5 mm.	0%	70
1.0-1.5 mm.	16%	
0.7-1.0 mm.	66%	
0.5-0.7 mm.	15%	
0.3-0.5 mm.	2%	
0.2-0.3 mm.	1%	75
Less than 0.2 mm.	0%	

The suspension is filtered through a coarse-meshed filter cloth, light aperture 0.3-0.5 mm. and having a filtering area of about 0.01 sq. m. per kgm of suspension. The pressure drop during the straining is equivalent to 40-50 mm. Hg. The straining period is about 6 seconds, reckoned from the moment straining begins, until the crystal mass becomes dry on the surface.

EXAMPLE 2.

Starting material and procedure as in Example 1, with the difference that 5 gms calcium nitrate dust is added.

A crystal mass is then obtained having the following granular distribution:

Exceeding 1.0 mm.	0%	
0.7-1.0 mm.	69%	
0.5-0.7 mm.	22%	
0.3-0.5 mm.	6%	95
0.2-0.3 mm.	2%	
Less than 0.2 mm.	1%	

Under the conditions stated in Example 1 a straining time of about 12 seconds is obtained.

From this Example it appears that an increase of the number of grains in the seed crystals causes a reduction of the granular size in the crystal suspension and consequently the straining time increases.

EXAMPLE 3.

Starting material and procedure as in Example 1, with the difference that the solution is cooled 7 degrees centigrade below the saturation temperature, whereupon 0.5 gms calcium nitrate dust is added.

A crystal mass is obtained having the following granular distribution:

Exceeding 1.0 mm.	0%	
0.7-1.0 mm.	60%	115
0.5-0.7 mm.	25%	
0.3-0.5 mm.	10%	
0.2-0.3 mm.	3%	
Less than 0.2 mm.	2%	

Under the conditions stated in Example 1 a straining period of about 18 seconds is obtained.

From the example it appears that increase of the degree of super-cooling of the solution at the time the seed crystals are added, causes reduction of the granular size and increase of the straining period.

EXAMPLE 4.

Starting material and procedure as in Example 1, with the difference that the

solution is only cooled 1 degree centigrade below saturation temperature, whereupon 0.5 gms calcium nitrate dust is added.

A crystal mass is then obtained having the following granular distribution:

	Exceeding 1.5 mm.	20%
	1.0-1.5 mm.	33%
	1.7-1.0 mm.	27%
	0.5-0.7 mm.	12%
10	0.3-0.5 mm.	5%
	0.2-0.3 mm.	2%
	Less than 0.2 mm.	1%

The maximum size of grain in the crystal mass is greater than 2.0 mm., and only 72% of the crystals have a granular size between 0.5 and 1.5 mm. The crystal mass is therefore coarse-grained and heterogeneous in size of grain. Under the conditions stated in Example 1 it cannot be strained at all. From the example it appears that the solution was not sufficiently sub-cooled at the time the seed crystals were added.

EXAMPLE 5.

Cola phosphate (CaO content approximately 51.5% by weight) is continuously dissolved in nitric acid. Quantitative ratio of raw phosphate to HNO_3 and acid strength are as stated in Example 1. The solution passes continuously through a container in which it is kept cooled to a temperature which provides crystallisation of such quantities of calcium nitrate as it is desired to remove from the solution. This temperature can in the crystallisation of tetrahydrate, for example, be 15°C .

A crystal mass is produced having the following granular distribution:

	Exceeding 3.0 mm.	0%
	2.0-3.0 mm.	10%
40	1.5-2.0 mm.	19%
	1.0-1.5 mm.	38%
	0.7-1.0 mm.	18%
	0.5-0.7 mm.	7%
	0.3-0.5 mm.	5%
45	0.2-0.3 mm.	2%
	Less than 0.2 mm.	1%

This crystal mass has a relatively high average size of grain and does not satisfy the requirements for uniform granular size. Under the conditions stated in Example 1 the suspension is found to be wholly unsuitable for straining.

EXAMPLE 6.

The process according to the invention can also be used for crystallisation of the compound $\text{NH}_4\text{NO}_3 \cdot 5\text{Ca}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O}$, which is formed when the nitric acid used contains ammonium ions in adequate quantities. Example 1 above in this case is effected as follows:

1 kgm Cola phosphate is dissolved in 2.3 kgms nitric acid containing 61% by weight HNO_3 and 7% by weight NH_4NO_3 . The solution is cooled to a temperature which is 55 degrees centigrade below the saturation

temperature, whereupon 0.5 gm calcium nitrate dust is added. The solution is cooled further to a temperature which gives crystallisation of the amount of double salt it is desired to remove from the solution, e.g., $70-25^\circ\text{C}$.

A crystal mass is obtained having a granular distribution and straining properties as indicated in Example 1.

What we claim is:—

1. A process for the crystallisation of calcium nitrates, from a nitric acid solution of calcium phosphate by cooling a solution of impure calcium phosphate in nitric acid, which solution may also contain an ammonium salt, and separation of the nitrate crystals from the mother lye and the finely divided impurities contained therein, by straining through a coarse-meshed filtering cloth, characterised in that the solution is cooled in batches and the crystallisation in each batch initiated by the addition of seed crystals the main content of which is calcium nitrate, at the point of time when the temperature of the solution is between 2 and 10 degrees centigrade below the saturation temperature, whereby the main body of the crystals produced has a granular size less than 2 mm., while at the same time at least 80% by weight of the crystals produced have a granular size between 0.5 and 1.5 mm., preferably between 0.5 and 1.0 mm.

2. A process according to Claim 1, 100 characterised in that the whole quantity of seed crystals is added simultaneously and in a very finely divided form (dust).

3. A process according to Claim 1 or Claim 2 whereby calcium nitrate is crystallised out, characterised in that ordinary nitrate of lime is used as seed crystals.

4. A process according to Claims 1, 2 or 3, whereby calcium nitrate tetrahydrate is crystallised out, characterised in that the calcium phosphate is dissolved in 55-60% by weight, preferably 58%, nitric acid, and that the seed crystals are added at a point of time, when the temperature of the solution is 4-7 degrees centigrade below the saturation temperature.

5. A process according to Claim 1 or Claim 2 or Claim 3, characterised in that in the presence of ammonium salt the double salt $5\text{Ca}(\text{NO}_3)_2 \cdot \text{NH}_4\text{NO}_3 \cdot 10\text{H}_2\text{O}$ is crystallised out.

6. A process according to any one of Claims 1 to 5, characterised in that the average size of grain in the crystals is regulated by varying the number of grains in the seed crystals.

7. A process according to any one of the preceding claims, characterised in that the crystallised calcium nitrate suspension is strained through a filtering cloth having 130

light apertures of the order of 0.3-0.5 mm.

8. A process for the crystallisation of nitrate from a nitric acid solution of calcium phosphate substantially as hereinbefore described with reference to any one of the foregoing Examples numbered 1, 2, 3, and 6.

9. Crystallised calcium nitrate, when pro-

duced by the process claimed in any one of the preceding claims.

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